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Sep 20, 1988

US-PAT-NO: 4772940

DOCUMENT-IDENTIFIER: US 4772940 A

TITLE: Polymer having isothianaphthene structure and electrochromic display

DATE-ISSUED: September 20, 1988

INVENTOR-INFORMATION:

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US-CL-CURRENT: 348/803; 136/256, 136/263, 204/291, 429/111, 429/122, 429/128

CLAIMS:

We claim:

1. An electrochromic display wherein a high molecular weight conductive membrane formed on a conductive transparent base is used as a display base and an opposing electrode is arranged thereunder via a liquid electrolyte, said high molecular weight conductive membrane comprising a polymer having an isothianaphthene structure and capable of being reversibly oxidized or reduced.

2. The electrochromic display of claim 1 wherein said isothianaphthene polymer has a structural formula selected from the group consisting of (Ia) and (Ib):
 ##STR11## wherein said R.sup.1 and R.sup.2 are selected independently from the group consisting of hydrogen atoms and hydrocarbon residues having 1 to 5 carbon atoms, with the proviso that said R.sup.1 and R.sup.2 may link together to form, along with the benzene ring, a fused ring which is naphthalene; said X is selected from the group consisting of sulfur, selenium and tellurium; said Y.sup.- represents an anion of an electrolyte; said z represents a number from 0.01 to 1 showing a ratio of the anion per mole of a monomer; and said n represents a number of from 5 to 500 showing a degree of polymerization.

3. The electrochromic display of claim 2 wherein X is sulfur.

4. The electrochromic display of claim 3 wherein R.sup.1 and R.sup.2 are both hydrogen.

5. The electrochromic display of claim 2 wherein R.sup.1 and R.sup.2 are selected independently from the group consisting of hydrogen, methyl and ethyl.

6. The electrochromic display of claim 2 wherein R.sup.1 and R.sup.2 are selected independently from the group consisting of hydrogen, methyl, methoxy and thiomethyl.

7. The electrochromic display of claim 2 wherein said polymer has the structure of formula (Ib) and X is sulfur.

8. The electrochromic display of claim 7 wherein Y.sup.- is selected from the group consisting of Cl.sup.-, Br.sup.-, I.sup.-, ClO.sub.4.sup.-, BF.sub.4.sup.-, PF.sub.6.sup.-, AsF.sub.6.sup.-, SbF.sub.6.sup.-, AlCl.sub.4.sup.-, AlBr.sub.4.sup.-, FeCl.sub.4.sup.- and CF.sub.3SO.sub.3.sup.-.

9. The electrochromic display of claim 7 wherein Y.sup.- is HSO.sub.4.sup.-.

10. The electrochromic display of claim 1 wherein z represents a number from 0 to 0.40.

11. The electrochromic display of claim 2 wherein said polymer membrane is formed on said display base by electrochemical polymerization thereon of a

compound having the formula ##STR12##

12. The electrochromic display of claim 1 wherein the thickness of said polymer membrane is from about 0.03 to about 30 μm .

13. The electrochromic display of claim 12 wherein the thickness of said polymer membrane is from about 0.05 to about 22 μm .

14. The electrochromic display of claim 13 wherein the thickness of said polymer membrane is from about 0.1 to about 10 μm .

15. The electrochromic display of claim 1 wherein said liquid electrolyte is a dispersion or solution comprising a supporting electrolyte in a solvent.

16. The electrochromic display of claim 15 wherein said supporting electrolyte comprises at least one compound of the formula $Z^{\text{sup.}} + Y^{\text{sup.}}$ wherein Z is a cation selected from the group consisting of alkali metal, quaternary ammonium, phosphonium, carbonium, pyrylium and pyridinium ions. and wherein Y is an anion selected from the group consisting of $\text{Cl}^{\text{sup.}}$, $\text{Br}^{\text{sup.}}$, $\text{I}^{\text{sup.}}$, $\text{ClO}_4^{\text{sup.}}$, $\text{BF}_4^{\text{sup.}}$, $\text{PF}_6^{\text{sup.}}$, $\text{AsF}_6^{\text{sup.}}$, $\text{SbF}_6^{\text{sup.}}$, $\text{AlCl}_4^{\text{sup.}}$, $\text{AlBr}_4^{\text{sup.}}$, $\text{FeCl}_4^{\text{sup.}}$ and $\text{CF}_3\text{SO}_3^{\text{sup.}}$, $\text{HSO}_4^{\text{sup.}}$ and $\text{HF}_2^{\text{sup.}}$.

17. The electrochromic display of claim 15 wherein said solvent is a nonaqueous organic solvent.

18. The electrochromic display of claim 17 wherein said solvent is aprotic and has a high dielectric constant.

19. The electrochromic display of claim 18 wherein said solvent is selected from the group consisting of ethers, ketones, nitriles, amines, amides, sulfur compounds, phosphoric ester compounds, phosphorous ester compounds, boric ester compounds, chlorinated hydrocarbons, esters, carbonates, nitro compounds and combinations thereof.

20. The electrochromic display of claim 19 wherein said solvent is selected from the group consisting of tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, acetonitrile, propionitrile, 4-methyl-2-pentanone, butyronitrile, valeronitrile, benzonitrile, 1,2-dichloroethane, γ -butyrolactone, valerolactone, dimethoxyethane, methylformate, propylene carbonate, ethylene carbonate, dimethylformamide, dimethyl sulfoxide, ethyl phosphate, methyl phosphate, ethyl phosphite, methyl phosphite, 3-methylsulfolane, and combinations thereof.

21. The electrochromic display of claim 15 wherein the concentration of said support electrolyte in said solvent is from about 0.001 to about 10 mole/l.

22. The electrochromic display of claim 1 wherein said polymer membrane is spaced apart from said opposing electrode at a distance of from about 0.05 to about 5 mm.

23. An electrode comprising a support member coated with polyisothianaphthene.

24. A battery comprising an anode and a polyisothianaphthene-coated cathode separated from the anode by a porous partitioning membrane.

25. A solar energy conversion device having a surface membrane material that is rendered conductive upon absorption of light, the surface membrane material comprising polyisothianaphthene.